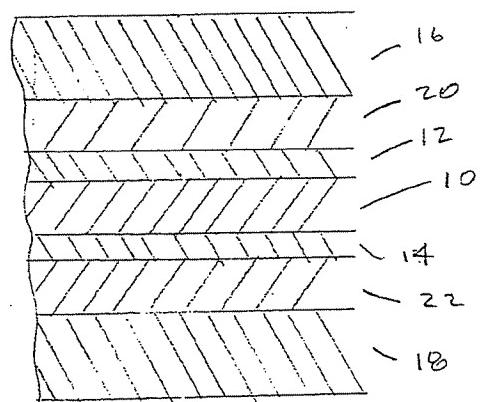


842600

~~101~~

FIG. 1

GAV  
154





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POSTAL SERVICE AS FIRST CLASS MAIL POSTAGE  
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COMMISSIONER OF PATENTS AND TRADEMARKS,  
WASHINGTON, D.C. 20231  
ON JULY 1, 1986

Mark B. Quatt

MARK B. QUATT  
REGISTRATION NO. 30,484

JULY 1, 1986

DATE

15D 4-11-86

15X

030

#2/LAK  
7-24-86

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Gautam P. Shah

Group Art Unit: 154

Serial No.: 842,600

Examiner: *Herbst*

Filed: March 21, 1986

Docket: 41259

For: Oxygen Barrier Oriented Shrink Film

**RECEIVED**

JUL 14 1986

GROUP 150

Honorable Commissioner of  
Patents and Trademarks  
Washington, D. C. 20231

Sir:

Pursuant to 37 CFR 1.56 and in accordance with 37 CFR section 1.97 et seq. Applicant, through and by his attorneys, hereby wishes to direct the Examiner's attention to the hereinafter discussed documents.

A filled in PTO-1449 form listing all of the documents listed below is presented herewith for the Examiner's review and convenience. Copies of the listed documents are enclosed. Each of these references appear to be relevant and/or material to the present application for the reasons given below.

U. S. Patent No. 4,284,674 issued to Sheptak appears to disclose a multilayer film having a core layer of ethylene vinyl alcohol copolymer adhered on each side to nylon, each nylon layer in turn being adhered to a chemically modified polyolefin, and a further layer of primer material suitable to adhere the modified polyolefin to an outer layer of polypropylene or other material suitable for conveying toughness, flex crack resistance and moisture barrier properties to the multi-ply film.

404/860625/3/1

U. S. Patent No. 4,355,721 issued to Knott et al appears to disclose a coextruded multilayer sheet having a first layer of nylon, and EVOH barrier layer, another layer of nylon, an adhesive layer, and another outside layer of, for example, high density polyethylene.

U. S. Patent No. 4,398,635 issued to Hirt appears to disclose a medication package in which a coextruded multiple layer sheet may have a structure including a layer of ethylene vinyl alcohol copolymer sandwiched between adjacent layers of nylon, and in which one of the nylon layers may be further adhered to a tie resin. The nylon layers may form either an outside surface or, in one example, internal layers with additional layers of polymeric materials added to each side of the sandwich structure.

U. S. Patent No. 4,400,428 issued to Rosenthal et al appears to disclose a composite film having a biaxially oriented polypropylene base film laminated on at least one surface with a multilayer structure including a gas barrier layer of a hydrolyzed ethylene vinyl acetate copolymer and a layer adjacent to the base film, and a heat sealable outer layer which may be, for example, modified propylene/ethylene copolymer. Adhesion promoting layers of modified polyolefin may include polypropylene containing grafted units of alpha, beta monounsaturated dicarboxylic acids.

U. S. Patent No. 4,407,873 issued to Christensen et al appears to disclose a packaging material for retort applications including a heat seal layer of linear low density polyethylene, a second layer of linear low density polyethylene with optionally 0% to 80% medium density polyethylene blended into the second layer, a third layer of anhydride modified medium density polyethylene, a fourth layer of nylon, a fifth layer of ethylene vinyl alcohol copolymer, and a sixth layer of nylon.

404/860625/3/2

U. S. Patent No. 4,421,823 issued to Theisen et al appears to disclose a flexible wrapping material of limited construction having a biaxially oriented polypropylene/oxygen barrier substrate, in which the oxygen barrier material may be EVOH; an extrusion laminate of a biaxially oriented polymer such as polypropylene or nylon, bonded to polyethylene; and a layer of heat sealable polymeric material such as ethylene vinyl acetate copolymer laminated to the substrate. A special polymer which may be, for example, polyethylene or ethylene vinyl acetate copolymer is bonded to one surface of the biaxially oriented polypropylene.

U. S. Patent No. 4,457,960 issued to Newsome appears to disclose a multilayer film having a core layer of a barrier material such as EVOH and EVOH blends. This film may be shrinkable and may be melt extruded, and may contain outside layers having a blend of linear low density polyethylene and ethylene vinyl acetate copolymer.

U. S. Patent No. 4,464,443 issued to Farrell et al appears to disclose the use of EVOH in a five layer structure having outside layers of high density polyethylene and intermediate layers of Plexar adhesive.

U. S. Patent No. 4,495,249 issued to Ohya et al appears to disclose a five layer film having a core layer of saponified copolymer of ethylene and vinyl acetate, two outer layers of a mixture of linear low density polyethylene and ethylene vinyl acetate copolymer, and two adhesive layers disposed between the core layer and outer layers.

U. S. Patent No. 4,501,797 issued to Super et al appears to disclose an unbalanced oriented multiple layer film including a first layer of polypropylene, a second layer of an anhydride modified polypropylene, and a third layer of ethylene vinyl alcohol copolymer.

U. S. Patent No. 4,501,798 issued to Koschak et al appears to disclose the use of a blend of EVOH and nylon in an unbalanced multiple layer polymeric film, also including either linear low density polyethylene or ethylene vinyl acetate copolymer in a sealant layer. Adhesive layers of preferably anhydride derivatives are also present.

404/860625/3/3

U. S. Patent No. 4,514,465 issued to Schoenberg appears to disclose a five layer thermoplastic film having surface layers comprising a four component blend of linear low density polyethylene, linear medium density polyethylene, ethylene vinyl acetate copolymer and at least one ultraviolet light stabilizer.

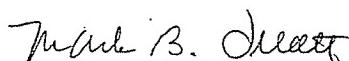
U. S. Patent No. 4,557,780 issued to Newsome et al appears to disclose a five layer thermoplastic film having a barrier layer of a blend of ethylene vinyl alcohol copolymer and nylon, adhesive layers on either side of the barrier layer, and fourth and fifth layers comprising 40 to 100% ethylene vinyl acetate copolymer and 0 to 60% linear low density polyethylene.

By inclusion of any given document in this Information Disclosure Statement Applicant in no way admits that such document is effective as prior art against the above-identified application under either 35 USC section 102 or 35 USC section 103.

The Examiner is requested to independently review each of the cited references for their relevance to the present case.

Please charge any additional prosecutorial fees which may be due to Grace deposit account no. 07-1765.

Respectfully submitted,



Mark B. Quatt  
Attorney for Applicants  
Registration No. 30,484

W. R. Grace & Co.  
Cryovac Division  
P. O. Box 464  
Duncan, S. C. 29334  
(803) 433-2817

404/860625/3/4

FORM PTO-1449 (REV. 7-80)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTY. DOCKET NO.	SERIAL NO.
				41259	842,600
				APPLICANT	
				Gautam P. Shah	
				FILING DATE	GROUP
				March 21, 1986	154
Sheet 1 of 2					
LIST OF PRIOR ART CITED BY APPLICANT (Use several sheets if necessary)					
MAIL JUL 30 1986					
U.S. PATENT DOCUMENTS					
EXAMINER'S INITIAL	DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS
THH	4,384,674		Shostak		
	4,355,721		Knott et al		
	4,398,635		Hilt		
	4,400,428		Rosenthal et al		
	4,407,873		Christensen et al		
	4,421,823		Theisen et al		
	4,457,960		Newcome		
	4,464,443		Farrell et al		
	4,495,249		Onya et al		
	4,501,797		Super et al		
	4,501,798		Kochak et al		
FOREIGN PATENT DOCUMENTS					
	DOCUMENT NUMBER	DATE	COUNTRY	CLASS	SUBCLASS
AL					
AM					
AN					
AO					
AP					
OTHER PRIOR ART (Including Author, Title, Date, Pertinent Pages, Etc.)					
AR					
AS					
AT					
EXAMINER:			DATE CONSIDERED	Nov 6, 1986	
<small>*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.</small>					

references cited on 892 attach to #5

FORM PTO-1449 (REV. 7-80)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTY. DOCKET NO.	SERIAL NO.	
				41259	842,600	
		APPLICANT		Ganjam P. Shah		
		FILING DATE		March 21, 1986	GROUP 154	
LIST OF PRIOR ART CITED BY APPLICANT (Use several sheets if necessary)						
U.S. PATENT DOCUMENTS						
EXAMINER INITIAL	DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE
AA	4,514,465		Schoenberg			
AB	4,557,780		Newcome et al			
AC						
AD						
AE						
AF						
AG						
AH						
AI						
AJ						
AK						
FOREIGN PATENT DOCUMENTS						
	DOCUMENT NUMBER	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION YES    NO
AL						
AM						
AN						
AO						
AP						
OTHER PRIOR ART (Including Author, Title, Date, Pertinent Pages, Etc.)						
AR						
AS						
AT						
EXAMINER <i>J. Herbert Jr.</i>						DATE CONSIDERED <i>Nov. 6, 1986</i>
<small>*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.</small>						

USCOMW-DC 80-3755



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Mark B. Quatt  
MARK B. QUATT  
REGISTRATION NO. 30,484

OCTOBER 9, 1986  
DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Gautam P. Shah

Group Art Unit: 154

Serial No.: 842,600

Examiner: *J.W.C.*

Filed: March 21, 1986

Docket: 41259

For: Oxygen Barrier Oriented Shrink Film

*RECEIVED*  
*3/6/86*  
*11/9/86*

INFORMATION DISCLOSURE STATEMENT

*OCT 21 1986*  
*GROUP 150*

Honorable Commissioner of  
Patents and Trademarks  
Washington, D. C. 20231

Sir:

Pursuant to 37 CFR 1.56 and in accordance with 37 CFR section 1.97 et. seq. Applicant, through and by his attorneys, hereby wishes to direct the Examiner's attention to the hereinafter discussed documents.

A filled in PTO-1449 form listing all of the documents listed below is presented herewith for the Examiner's review and convenience. Copies of the listed documents are enclosed. Each of these references appear to be relevant and/or material to the present application for the reasons given below.

U. S. Patent No. 4,182,457 issued to Yamada et al appears to disclose multi-layer containers of for example 5 and 7 layers, having intermediate layers of ethylene vinyl alcohol copolymer or nylon, adhesive layers of carboxylic acid-modified polypropylene or ethylene propylene copolymer, and outside layers of polypropylene, ethylene propylene copolymer, or polyolefins.

404/861006/9/1

U. S. Patent No. 4,405,667 issued to Christensen et al appears to disclose a retortable pouch having a linear low density polyethylene heat seal layer, a second layer of a blend of linear low density polyethylene and propylene ethylene copolymer, optional third, fourth, and fifth layers of propylene ethylene copolymer, a sixth layer of an anhydride modified polypropylene, a seventh layer of nylon, an eighth layer of ethylene vinyl alcohol copolymer and a ninth layer of nylon.

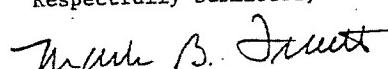
U. S. Patent No. 4,588,648 issued to Krueger et al appears to disclose a multiple layer plastic film having polypropylene adhered to nylon by an intermediate layer of a blend of an ungrafted propylene-based polymer and a graft copolymer of maleic anhydride onto an olefin polymer or copolymer, with additional layers of nylon, ethylene vinyl alcohol copolymer, and nylon.

By inclusion of any given document in this Information Disclosure Statement Applicant in no way admits that such document is effective as prior art against the above-identified application under either 35 USC section 102 or 35 USC section 103.

The Examiner is requested to independently review each of the cited references for their relevance to the present case.

Please charge any additional prosecutorial fees which may be due to Grace deposit account no. 07-1765.

Respectfully submitted,



Mark B. Quatt  
Attorney for Applicants  
Registration No. 30,484

W. R. Grace & Co.  
Cryovac Division  
P. O. Box 464  
Duncan, S. C. 29334  
(803) 433-2817

404/861006/9/2



## UNITED STATES DEPARTMENT OF COMMERCE

Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.

EXAMINER	
ART UNIT	PAPER NUMBER
4	

DATE MAILED:

## EXAMINER INTERVIEW SUMMARY RECORD

All participants (applicant, applicant's representative, PTO personnel):

(1) Mark Deatt (3) \_\_\_\_\_  
 (2) \_\_\_\_\_ (4) \_\_\_\_\_

Date of interview Nov 4, 1986Type:  Telephonic  Personal (copy is given to  applicant:  applicant's representative).Exhibit shown or demonstration conducted:  Yes  No. If yes, brief description: \_\_\_\_\_Agreement  was reached with respect to some or all of the claims in question.  was not reached.Claims discussed: All

Identification of prior art discussed: \_\_\_\_\_

Description of the general nature of what was agreed to if an agreement was reached, or any other comments: Restriction:I Claims 1-23, multilayer product, 428/426.3P Claims 24-28 method of coextruding  
156-244.11 Applicant elected Group I Traverse.

(A fuller description, if necessary, and a copy of the amendments, if available, which the examiner agreed would render the claims allowable must be attached. Also, where no copy of the amendments which would render the claims allowable is available, a summary thereof must be attached.)

Unless the paragraphs below have been checked to indicate to the contrary, A FORMAL WRITTEN RESPONSE TO THE LAST OFFICE ACTION IS NOT WAIVED AND MUST INCLUDE THE SUBSTANCE OF THE INTERVIEW (e.g., items 1-7 on the reverse side of this form). If a response to the last Office action has already been filed, then applicant is given one month from this interview date to provide a statement of the substance of the interview.

 It is not necessary for applicant to provide a separate record of the substance of the interview. Since the examiner's interview summary above (including any attachments) reflects a complete response to each of the objections, rejections and requirements that may be present in the last Office action, and since the claims are now allowable, this completed form is considered to fulfill the response requirements of the last Office action.

Thomas J. Herbert  
Examiner's Signature

PTOL-413 (rev. 1-81)

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UNITED STATES DEPARTMENT OF COMMERCE  
Patent and Trademark Office

Address: COMMISSIONER OF PATENTS AND TRADEMARKS  
Washington, D.C. 20231

SERIAL NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTORNEY DOCKET NO.
06/842,600	03/21/86	SHAH	G 11259

W. R. GRACE & CO.  
CRYOVAC DIVISION  
PATENT DEPT.  
P.O. BOX 464  
DUNCAN, SC 29334

EXAMINER	
HERBERT JR. T	
ART UNIT	PAPER NUMBER
154	5
DATE MAILED:	
11/20/86	

This is a communication from the examiner in charge of your application.

COMMISSIONER OF PATENTS AND TRADEMARKS

This application has been examined       Responsive to communication filed on \_\_\_\_\_       This action is made final.

A shortened statutory period for response to this action is set to expire 3 month(s), 0 days from the date of this letter.  
Failure to respond within the period for response will cause the application to become abandoned. 35 U.S.C. 133

Part I THE FOLLOWING ATTACHMENT(S) ARE PART OF THIS ACTION:

- 1.  Notice of References Cited by Examiner, PTO-892.
- 2.  Notice re Patent Drawing, PTO-948.
- 3.  Notice of Art Cited by Applicant, PTO-149
- 4.  Notice of informal Patent Application, Form PTO-152
- 5.  Information on How to Effect Drawing Changes, PTO-1474
- 6.

Part II SUMMARY OF ACTION

1.  Claims 1-28 are pending in the application.

Of the above, claims 24-28 are withdrawn from consideration.

2.  Claims \_\_\_\_\_ have been cancelled.

3.  Claims \_\_\_\_\_ are allowed.

4.  Claims 1-23 are rejected.

5.  Claims \_\_\_\_\_ are objected to.

6.  Claims 1-28 are subject to restriction or election requirement.

7.  This application has been filed with informal drawings which are acceptable for examination purposes until such time as allowable subject matter is indicated.

8.  Allowable subject matter having been indicated, formal drawings are required in response to this Office action.

9.  The corrected or substitute drawings have been received on \_\_\_\_\_. These drawings are  acceptable;  not acceptable (see explanation).

10.  The  proposed drawing correction and/or the  proposed additional or substitute sheet(s) of drawings, filed on \_\_\_\_\_, has (have) been  approved by the examiner.  disapproved by the examiner (see explanation).

11.  The proposed drawing correction, filed \_\_\_\_\_, has been  approved.  disapproved (see explanation). However, the Patent and Trademark Office no longer makes drawing changes. It is now applicant's responsibility to ensure that the drawings are corrected. Corrections MUST be effected in accordance with the instructions set forth on the attached letter "INFORMATION ON HOW TO EFFECT DRAWING CHANGES", PTO-1474.

12.  Acknowledgment is made of the claim for priority under 35 U.S.C. 119. The certified copy has  been received  not been received \_\_\_\_\_.

been filed in parent application, serial no. \_\_\_\_\_; filed on \_\_\_\_\_.

13.  Since this application appears to be in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under Ex parte Quayle, 1935 C.D. 11; 453 O.G. 213.

14.  Other \_\_\_\_\_

Serial No. 842,600

-2-

Art Unit 154

15.

Restriction to one of the following inventions is required under 35 U.S.C. 121:

I. Claims 1-23, drawn to a multilayer article, classified in Class 428, subclass 476.3.

II. Claims 24-28, drawn to a method of coextruding, classified in Class 156, subclass 244.11.

16.

The inventions are distinct, each from the other, because of the following reasons:

Inventions II and I are related as process of making and product made.

The inventions are distinct if either (1) the process as claimed can be used to make another and materially different product, or (2) the product as claimed can be made by another and materially different process. MPEP 806.05(f).

In this case, the product as claimed can be made by a materially different process such as by laminating pre-formed layers together.

17.

Because these inventions are distinct for the reasons given above and have acquired a separate status in the art as shown by their different classification, restriction for examination purposes as indicated is proper.

18.

During a telephone conversation with applicant's attorney, Mr. Mark Quatt on November 5, 1986 a

Serial No. 842,600

-3-

Art Unit 154

provisional election was made with traverse to prosecute the invention of Group I, claims 1-23. Affirmation of this election must be made by applicant in responding to this Office action. Claims 24-28 are withdrawn from further consideration by the examiner as being drawn to a nonelected invention. See 37 CFR 1.142(b).

19.

The following is a quotation of 35 U.S.C. 103 which forms the basis for all obviousness rejections set forth in this Office action:

A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Subject matter developed by another person, which qualifies as prior art only under subsection (f) and (g) of section 102 of this title, shall not preclude patentability under this section where the subject matter and the claimed invention were, at the time the invention was made, owned by the same person or subject to an obligation of assignment to the same person.

20.

Claims 1-23 are rejected under 35 U.S.C. 103 as being unpatentable over Sheptak or Hirt in view of Mueller.

Each of Sheptak and Hirt discloses a multilayered film comprising EVOH core with intermediate polyamide (e.g. nylon layers which in turn carry out polymeric

Serial No. 842,600

-4-

Art Unit 154

layers such as polyolefin blends as shown in Sheptak. With Mueller further showing multilayered film structures having outer layers of polyolefin blends, e.g. LLDPE with LDPE, ethylene/propylene copolymer, etc, it would be obvious to employ these outer layers of Mueller as the outer layers in Sheptak or Hirt.

21.

Knott et al., Rosenthal et al., Christensen et al., Theisen et al., Newsome, Farrell et al., Ohya et al., Super et al., Kaschak et al., Schoenberg and Newsome et al. -cited by applicant- are made of record as of interest. Note pages 2-4 of the specification and information statement by applicant' July 3, 1986.

TJHerbert:bh  
(703) 557-6525  
11/18/86

THOMAS J. HERBERT  
PRIMARY EXAMINER  
ART UNIT 154

PTO - 948  
(Rev. 8-82)U.S. DEPARTMENT OF COMMERCE  
PATENT AND TRADEMARK OFFICE

GROUP 154

ATTACHMENT TO PAPER NUMBER	5
S.N.	842600

## NOTICE OF PATENT DRAWINGS OBJECTION

Drawing Corrections and/or new drawings may only be submitted in the manner set forth in the attached letter, "Information on How to Effect Drawing Changes" PTO-1474.

- A.  The drawings, filed on 3/21/86, are objected to as informal for reason(s) checked below:

- 1.  Lines Pale.
- 2.  Paper Poor.
- 3.  Numerals Poor.  
*Pencil dry*
- 4.  Lines Rough and Blurred.
- 5.  Shade Lines Required.
- 6.  Figures Must be Numbered.
- 7.  Heading Space Required.
- 8.  Figures Must Not be Connected.
- 9.  Criss-Cross Hatching Objectionable.
- 10.  Double-Line Hatching Objectionable.
- 11.  Parts in Section Must Be Hatched.
- 12.  Solid Black Objectionable.
- 13.  Figure Legends Placed Incorrectly.
- 14.  Mounted Photographs.
- 15.  Extraneous Matter Objectionable.  
[37 CFR 1.84 (1)]
- 16.  Paper Undersized; either 8½" x 14", or 21.0 cm. x 29.7 cm. required.
- 17.  Proper A4 Margins Required:  
 TOP 2.5 cm.    RIGHT 1.5 cm.  
 LEFT 2.5 cm.    BOTTOM 1.0 cm.
- 18.  Other:  
*pencil dry req'd*

- B.  The drawings, submitted on 3/21/86, are so informal they cannot be corrected. New drawings are required. Submission of the new drawings MUST be made in accordance with the attached letter.

U.S. DEPARTMENT OF COMMERCE  
PATENT AND TRADEMARK OFFICE

Attachment to Paper Number	5
Serial No.	842,600

#### INFORMATION ON HOW TO EFFECT DRAWING CHANGES

##### 1. Correction of Informalities (Draftsman's objections on PTO-948)

In order to correct any informalities in the drawings, applicants MUST comply with options (a) or (b) below. Failure to do so will result in ABANDONMENT of the application.

a) File new drawings with the changes incorporated therein. Applicant may delay filing of the new drawings until the application is allowed by the examiner. If delayed, the new drawings MUST be filed within the THREE MONTH statutory period set for payment of the base issue fee in the "NOTICE OF ALLOWANCE AND BASE ISSUE FEE DUE" (PTOL-85). Also, if delayed, the drawings should be filed as a separate paper with a transmittal letter addressed to the Official Draftsman and which indicates the following in the upper right hand corner:

Date of the Notice of Allowance  
Issue Batch Number  
Serial Number

b) Request a commercial bonded drafting firm (see list below) to make the necessary corrections.

A BONDED DRAFTSMAN MUST BE AUTHORIZED, THE CORRECTIONS EXECUTED AND THE CORRECTED DRAWINGS RETURNED TO THE OFFICE DURING THE THREE MONTH STATUTORY PERIOD SET FOR PAYMENT OF THE BASE ISSUE FEE IN THE "NOTICE OF ALLOWANCE AND BASE ISSUE FEE DUE" (PTOL-85). NOTE THAT THE STATUTE DOES NOT PERMIT EXTENSION OF THE THREE MONTH PERIOD SET TO PAY THE BASE ISSUE FEE.

##### 2. Corrections other than Informalities Noted by the Draftsman on the PTO-948.

All changes to the drawings, other than informalities noted by the Draftsman, MUST be made in the same manner as above except that, if delayed option (a) is selected, normally, a sketch of the changes to be incorporated into the new drawings MUST be approved by the examiner before the application will be allowed. If option (b) is selected, normally, applicants must submit, in duplicate, a separate paper containing a sketch of the proposed changes before the application will be allowed. No changes will be permitted to be made, other than correction of informalities, unless the examiner has approved the proposed changes.

##### 3. Listing of Bonded Draftsmen

SEE LIST ON REVERSE SIDE OF THIS FORM.

IT IS SUGGESTED THAT APPLICANTS DETACH THIS LETTER FROM THE OFFICE ACTION AND ATTACH IT TO THE FRONT OF APPLICANT'S FILE AS A REMINDER THAT, IN ORDER TO AVOID ABANDONMENT, A BONDED DRAFTSMAN MUST BE AUTHORIZED, THE CORRECTIONS EXECUTED AND THE CORRECTED DRAWINGS RETURNED TO THE OFFICE, OR NEW DRAWINGS SUBMITTED, DURING THE THREE MONTH STATUTORY PERIOD SET FOR PAYMENT OF THE BASE ISSUE FEE. NOTE THAT THE STATUTE DOES NOT PERMIT EXTENSION OF THE THREE MONTH PERIOD SET TO PAY THE BASE ISSUE FEE.

American Futures Design Company  
P.O. Box 365  
1400 Ramsey Drive  
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Washington, DC 20036-3399  
(202) 466-8800

Grapho-Tech  
11301 Rockville Pike  
Kensington, MD 20895  
(301) 881-9400

Ellsworth G. Jackson  
101 Rittenhouse St. NE  
Washington, DC 20011  
(202) 726-0908

Keithley Patent Drafting Svcs.  
1200 18th Street N.W.  
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Measured Drawings  
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Washington, DC 20005  
(202) 797-0666

Mil-R Productions  
2107 Mt. Vernon Ave.  
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Gerald M. Murphy  
P.O. Box 2098  
Eads Street Station  
Arlington, VA 22202  
(703) 521-1500

National Graphic Center  
205 W. Jefferson St.  
Falls Church, VA 22046  
(703) 533-8700

Oliver Patent Drafting Svcs.  
1205 Darlington St.  
Forestville, MD 20747  
(301) 336-0351

Ord-Marine Engineering  
10315 Kensington Pkwy.  
Kensington, MD 20895  
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Suite 700  
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Arlington, VA 22202  
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TO SEPARATE OLD TOP AND BOTTOM EDGES, SNAP-APART AND DISCARD CARBON

FORM PTO-892 (REV. 3-78)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		SERIAL NO.	GROUP ART UNIT	ATTACHMENT TO PAPER NUMBER	5	
NOTICE OF REFERENCES CITED				APPLICANT(S) <i>Shah</i>				
U.S. PATENT DOCUMENTS								
*	DOCUMENT NO.	DATE	NAME	CLASS	SUB-CLASS	FILING DATE IF APPROPRIATE		
V A	4 1 8 2 4 5 7	1-1980	<i>Yamada et al.</i>	428	354			
V B	4 4 0 5 6 6	7 9-1983	<i>Christensen et al.</i>	428	35			
V C	4 5 6 1 9 2 0	12-1985	<i>Foster</i>	156	24411			
V D	4 5 8 8 6 4 8 5	5-1986	<i>Krueger et al.</i>	428	4958	<i>6/30/84</i>		
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<i>1 of 4</i>								

**United States Patent [19]**

Yamada et al.

**4,182,457****Jan. 8, 1980****[54] MULTILAYER CONTAINER**

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[21] Appl. No.: 821,484

[22] Filed: Aug. 3, 1977

**[30] Foreign Application Priority Data**

Aug. 10, 1976 [JP]	Japan	51-94533
Jul. 18, 1977 [JP]	Japan	52-85114

[51] Int. Cl.<sup>2</sup> B32B 15/08; B32B 27/08  
 [52] U.S. Cl. 215/1 C; 220/453;  
 229/1.5 B; 426/127; 428/35

[58] Field of Search 428/35, 340, 474, 910;  
 215/1 C; 156/243, 244.11, 244.14, 244.22,  
 229/1.5; 106/324.1, 524.2, 524.3, 524.4, 524.5,  
 524.6, 524.7, 524.8; 220/453; 426/106, 126, 127,  
 129, 415

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**[57] ABSTRACT**

A transparent multi-layer container comprising a co-extrude of an oxygen-barrier resin layer and an orienting resin layer which is monoaxially or biaxially oriented is disclosed. An adhesive resin layer is preferably interposed between the oxygen-barrier layer and the orienting resin layer, and this co-extrudate is drawn and molded at a specific temperature determined relatively to the melting points and softening points of the respective resins. This container is excellent in the combination of transparency, rigidity, mechanical strength, gas-barrier property and interlaminar peel strength.

9 Claims, No Drawings

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**MULTILAYER CONTAINER****BACKGROUND OF THE INVENTION****(1) Field of the Invention**

This invention relates to a multi-layer plastic drawn and molded container excellent in transparency, rigidity, mechanical strength, water resistance and gas barrier property to oxygen and the like and having a practically satisfactory interlaminar peel strength under falling, shaking or impact, and to a process for the preparation of this excellent container.

**(2) Description of the Prior Arts**

It is well known that when a thermoplastic resin is drawn at a relatively low temperature, namely at a temperature lower than the melting point or softening point of the resin or a temperature just above the melting point or softening point of the resin, as a result of orientation of the polymer chain or crystal, such properties as rigidity, mechanical strength, gas barrier property and transparency can be improved. These improvements are practically utilized in biaxially drawn films, filaments, drawn tapes, biaxially drawn blow bottles and draw-molded cups.

In the field of narrow- and broad-mounted hollow plastic containers, for example, a biaxially drawn blow bottle of the vinylidene chloride resin type molded according to the method disclosed in Japanese Pat. Publication No. 8583/63 has heretofore been broadly used as a ketchup bottle because it has an excellent gas barrier property. However, because of generation of poisonous gases on burning or migration of the monomer or additive into the content, bottles of this type are hardly used at the present. Biaxially drawn blow bottles of polypropylene formed according to the principle, method and apparatus disclosed in Japanese Pat. Publication No. 16245/63, Japanese Patent Application Laid-Open Specification No. 3492/71, etc., have excellent transparency, rigidity and mechanical strength, and they are broadly used as bottles for shampoo or the like instead of polyvinyl chloride bottles in U.S.A. and as bottles for medicines, for example, Ringer's solution, instead of glass bottles in Japan. Further, broad-mouthed polypropylene cups prepared by solid-phase pressure forming at a relatively low temperature according to the method disclosed in Kunststoffe Bd. 65, 1975, H. 10, page 666 have now been attracting attentions as substitutes for polyvinyl chloride cups. Further, biaxially drawn blow bottles of polyethylene terephthalate disclosed in the specification of U.S. Pat. No. 3,733,309 have been test-marketed as bottles for carbonated drinks and now attract attentions in the art.

In case of the above-mentioned biaxially drawn blow bottles of the vinylidene chloride resin type, when a contained liquid, semi-liquid or pasty food has contact with the inner wall of the bottom, a problem of migration of the monomer or the like rises, and they cannot be regarded as practical semi-rigid containers. Biaxially drawn blow bottles of polypropylene and polypropylene cups prepared by solid phase pressure forming are inferior in the gas barrier property, and they cannot substantially be applied to foods of which the preservability is sensitive to oxygen permeating through the container wall. Although biaxially drawn blow bottles of polyethylene terephthalate have a relatively high gas barrier property and are very excellent in rigidity and transparency, when they are allowed to stand in an atmosphere maintained at 60° to 70° C. for 3 to 5 min-

utes, they show such thermal shrinkage as an empty volume shrinkage of 1 to 3%, a total height shrinkage of 0.4 to 0.8% and a barrel diameter shrinkage of 0.7 to 1.2%. Further, when they are allowed to stand in an atmosphere maintained at 80° C. for 1 minute, they are deformed to such an extent that they cannot be practically used. Accordingly, these bottles cannot be used when hot filling of contents is conducted or for storage of foods requiring heat sterilization, for example,

For the foregoing reasons, as in case of melt-molded containers, multi-layer structures in which defects of respective resins are compensated and which can meet practical demands are required in case of not only biaxially drawn blow molded containers prepared by forming a thermoplastic resin into a bottomed or bottomless parison and conducting the step of elongating the parison in the axial direction thereof at a relatively low temperature, for example, the melting point of the resin and the step of inflating the parison in a direction rectangular to the axial direction simultaneously or in this order (namely in sequence) but also biaxially drawn cups pressure-formed in the solid phase from a sheet at a relatively low temperature.

Drawn multi-layer containers are proposed in, for example, the specification of U.S. Pat. No. 3,733,309 and Japanese Patent Application Laid-Open Specification No. 32164/73, but these known drawn multi-layer containers are still insufficient from the practical viewpoint with respect to the interlaminar strength between every two adjacent layers, selection of constituent resin layers and selection of molding conditions such as the molding temperature and draw ratio. In addition, use of an unsaturated carboxylic acid-grafted thermoplastic resin as an adhesive improving the interlaminar peel strength has been proposed in, for example, Japanese Patent Application Laid-Open Specification No. 67384/76, but in this proposal, no sufficient regard is paid to the relation between the molding conditions such as the molding temperature and draw ratio and the adhesiveness.

**BRIEF SUMMARY OF THE INVENTION**

We found that in order to obtain biaxially drawn blow-molded bottles or draw-molded containers such as solid phase pressure-formed cups, which have a high barrier property to gases such as oxygen and are excellent in the combination of transparency, rigidity, mechanical strength and other physical properties, it is necessary to select very strictly constituent resin layers and molding conditions such as the molding temperature and draw ratio in view of the practical utility and moldability.

We also found that when a draw-molded container is prepared from a multi-layer structure comprising an oxygen-barrier thermoplastic resin layer and a layer of an orienting thermoplastic resin other than the oxygen-barrier thermoplastic resin preferably with an adhesive resin layer interposed between said two resin layers, in order to attain a high interlaminar peel strength, it is very important to select the respective resins so that a specific relation is established among the melting or softening points of the resins and to perform draw-molding at a temperature in a specific range.

In accordance with the present invention, there is provided a container having a multi-layer structure, which comprises a plurality of thermoplastic resins,

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wherein at least one layer of the container is composed of an oxygen-barrier thermoplastic resin having an oxygen permeability lower than  $5.5 \times 10^{-12}$  cc-cm/ $\text{cm}^2\text{-sec-cmHg}$  as measured at 37°C. and at least one of the remaining layers comprises an orienting thermoplastic resin other than the oxygen-barrier thermoplastic resin, said two resins are selected so that the requirement represented by the following formula:

$$(1) |T_B - T_O| \leq 35^\circ\text{C.}$$

wherein  $T_B$  stands for the melting or softening point (°C.) of said oxygen-barrier thermoplastic resin and  $T_O$  stands for the melting or softening point (°C.) of said orienting thermoplastic resin, is satisfied, and wherein at least one of two-dimensional orientation coefficients ( $l$  and  $m$ ) of at least one layer composed of said orienting thermoplastic resin in a smallest-thickness portion of the container is at least 0.05.

In accordance with the present invention, there is also provided a container having a multi-layer structure, which comprises at least one layer composed of an oxygen-barrier thermoplastic resin having an oxygen permeability lower than  $5.5 \times 10^{-12}$  cc-cm/ $\text{cm}^2\text{-sec-cmHg}$  as measured at 37°C., at least one layer comprising an orienting thermoplastic resin other than the oxygen-barrier thermoplastic resin and at least one layer interposed between said oxygen-barrier thermoplastic resin layer and said orienting thermoplastic resin layer and being composed of a resin having an adhesiveness to both of said resins, wherein said three resins are selected so that the requirements represented by the following formulae:

$$(1) |T_B - T_O| \leq 35^\circ\text{C.}$$

and

$$(2) 90^\circ\text{C.} \geq T_O - T_C \geq 2^\circ\text{C.}$$

wherein  $T_B$  stands for the melting or softening point (°C.) of said oxygen-barrier thermoplastic resin,  $T_O$  stands for the melting or softening point (°C.) of the melting or softening point of said orienting thermoplastic resin and  $T_C$  stands for the melting or softening point (°C.) of said adhesive resin, at least one of two-dimensional orientation coefficients ( $l$  and  $m$ ) of at least one layer composed of said orienting thermoplastic resin in a smallest-thickness portion of the container is at least 0.05, and wherein the layer of said adhesive resin is substantially non-oriented.

This invention will now be described in detail.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS Resin Components

In the container of this invention, in order to attain the foregoing objects, it is important that a gas-barrier resin having an oxygen permeability lower than  $5.5 \times 10^{-12}$  cc-cm/ $\text{cm}^2\text{-sec-cmHg}$  as measured at 37°C. and an orienting thermoplastic resin other than the gas-barrier resin should be selected and combined as the layer-constituting resin so that the difference ( $\Delta t = |T_B - T_O|$ ) between the melting or softening point ( $T_B$ ) of the gas-barrier resin and the melting or softening point ( $T_O$ ) of the orienting thermoplastic resin is smaller than 35°C., especially smaller than 10°C.

In the instant specification and appended claims, the melting point is defined as the thermodynamic primary

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transition point at which the crystal phase of a crystalline or semi-crystalline polymer is molten, as described in "Crystallization of Polymers" written by Leo Mandelkern and published by McGraw-Hill Book Company in 1964, and in general, the melting point can easily be determined according to the differential thermal analysis method, the specific heat-temperature curve method, the polarizing microscope method, the X-ray diffractometry method, the infrared absorption spectrum method or the like.

Further, in the instant specification and appended claims, the softening point corresponds to the thermodynamic secondary transition point, i.e., the glass transition point, at which a polymer is substantially softened. This softening point is described in, for example, "Physics of Polymers" compiled by Japanese Association of Physics and published by Asakura Shoten in 1963 and can easily be determined by the specific heat- or specific volume-temperature curve method, the differential thermal analysis method or the industrial test methods such as methods of ASTM D 648-56, ASTM D 1525-58T and ASTM D 569-48.

In general, melt-extrudable thermoplastic resins having a good gas-barrier property to gases such as oxygen and carbon dioxide gas, for example, ethylene-vinyl alcohol copolymers and nylon resins, contain polar groups such as hydroxyl groups and amide groups on the main or side chains of polymers. The melting or softening points of these resins vary broadly depending on the content of polar groups, the chemical composition and other factors.

As described in the specifications of U.S. Pat. Nos. 3,183,203 and 3,419,654, ethylene-vinyl alcohol copolymers can be obtained by saponifying a copolymer of ethylene or a combination of the majority of ethylene and the minority of other olefin such as propylene with a vinyl ester of a lower fatty acid such as vinyl formate, vinyl acetate, vinyl propionate or the like, especially an ethylene-vinyl acetate copolymer. It has been found that in ethylene-vinyl alcohol copolymer resins, the following relation is substantially established between the melting point ( $T_m$ ) determined according to the differential thermal analysis method or the like and the mole content (%) of ethylene:

$$(3) T_m = 1.64X + 68$$

wherein  $T_m$  stands for the melting point of an ethylene-vinyl alcohol copolymer having an ethylene content of 0 to 80 mole % and  $X$  stands for the vinyl alcohol content (mole %) in the copolymer.

It has also been found that in case of nylons of the ring opening polymerization type the melting point varies depending on the kind of the amino acid monomer, in case of nylons of the polycondensation type the melting point varies depends on the kind of the acid and the amine, in case of nylons of the copolymer type the melting point varies depending on the monomer composition, and that in case of nylon polymer blends the melting point varies depending on the polymer blending ratio. Melting points of these nylon type polymers as determined according to the differential thermal analysis method or the like are as shown in Table 1 given hereinafter.

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Table I

Resin	Melting Point (Tm), °C.
<b>Polyamides of Ring Opening Polymerization Type</b>	
α-Aminocaproic acid polymer (nylon 6)	223
α-Aminohexanoic acid polymer (nylon 7)	233
α-Aminocaprylic acid polymer (polymer 8)	200
α-Aminopalmitic acid polymer (nylon 9)	210
α-Aminodecanoic acid polymer (nylon 10)	188
α-Aminoundecanoic acid polymer (nylon 11)	185
α-Aminododecanoic acid polymer (nylon 12)	180
α-Aminotridecanoic acid polymer (nylon 13)	180
<b>Polyamides of Polycondensation Type</b>	
Polyhexamethylene adipamide (6,6-nylon)	265
Polyhexamethylene sebacamide (6,11-nylon)	185
Polyhexamethylene sebacamide (6,1-nylon)	225
Polyhexamethylene dodecamide (6,12-nylon)	212
Polyhexamethylene tridecamide (6,13-nylon)	204
Polydecamethylene hexadecamide (10,6-nylon)	225
Polydecamethylene sebacamide (10,10-nylon)	213
Polydecamethylene dodecamide (10,12-nylon)	195
Polydecamethylene tridecamide (10,13-nylon)	187
Polydodecamethylene adipamide (12,6-nylon)	210
Polydodecamethylene sebacamide (12,10-nylon)	190
Polydodecamethylene dodecamide (12,12-nylon)	185
Polytridecamethylene sebacamide (13,10-nylon)	170
Polytridecamethylene tridecamide (13,13-nylon)	174
<b>Nylons of Copolymer Type</b>	
6,6-Nylon-6,10-Nylon Copolymers	
6,6-nylon content of 0 mole %	225
6,6-nylon content of 20 mole %	202
6,6-nylon content of 30 mole %	192
6,6-nylon content of 40 mole %	195
6,6-nylon content of 60 mole %	210
6,6-nylon content of 80 mole %	233
6,6-nylon content of 100 mole %	265
6-Nylon-6,6-Nylon Copolymers	
6,6-nylon content of 0 mole %	223
6,6-nylon content of 20 mole %	163
6,6-nylon content of 40 mole %	156
6,6-nylon content of 60 mole %	170
6,6-nylon content of 80 mole %	220
6,6-nylon content of 100 mole %	265
<b>Nylon Polymer Blends</b>	
6-Nylon-6,6-Nylon Blends	
6,6-nylon mixing ratio of 0%	225
6,6-nylon mixing ratio of 20 mole %	215
6,6-nylon mixing ratio of 40 mole %	230
6,6-nylon mixing ratio of 60 mole %	248
6,6-nylon mixing ratio of 80 mole %	250
6,6-nylon mixing ratio of 100 mole %	265

As pointed out hereinbefore, in resins having a barrier property to a gas such as oxygen, for example, ethylene-vinyl alcohol copolymers and nylon resins, the melting or softening point varies depending on the content of a polar group such as a hydroxyl or amide group or the chemical composition.

Data of the oxygen permeability ( $\text{PO}_2$ ,  $\text{cc} \cdot \text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$ ) as determined at 37°C. in the absolute dry state of ethylene-vinyl alcohol copolymers and polyamides excellent in the barrier property to gases such as oxygen are shown in Table 2 given hereinafter.

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Table 2-continued

Resin	$\text{PO}_2 \times 10^{12}$ cc · cm <sup>2</sup> · sec · cmHg (at 37°C. and 0% RH)
Vinyl alcohol content of 70 mole %	0.07
Vinyl alcohol content of 80 mole %	0.04
<b>Polyamides</b>	
6-Nylon	4.0
10-E-Nylon	4.5
11-Nylon	4.9
12-Nylon	5.3
6,6-Nylon	0.69
6,10-Nylon	0.8
10,6-Nylon	0.61
15-6-Nylon-6,6-nylon copolymer (6-nylon content = 10 mole %)	1.0
6-Nylon-6,6-nylon copolymer (6-nylon content = 30 mole %)	2.0

20 In this invention, use of a thermoplastic resin having an oxygen permeability ( $\text{PO}_2$ ) lower than  $4.5 \times 10^{-12} \text{ cc} \cdot \text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$  as determined at 37°C. is preferred, and an ethylene-vinyl alcohol copolymer, especially a saponified ethylene-vinyl acetate copolymer having an ethylene content of 25 to 65 mole % and a degree of saponification of at least 99 mole %, is most preferred. Of course, nylon resins can also be used conveniently. These oxygen-barrier thermoplastic resins should, of course, have a molecular weight sufficient to form a film.

25 In this invention, in order to obtain a container comprising an oxygen-barrier resin layer (A) and an orienting resin layer (B), in which the orienting resin layer is effectively oriented and the adhesiveness between the two resin layers and the transparency as a whole are excellent, the two resins should be selected so that their melting or softening points satisfy the requirement represented by the above formula (1).

In general, when a parison or sheet having a multi-layer structure is subjected to draw molding or solid phase pressure forming, the interlaminar peel strength between two layers is drastically reduced. It is believed that the reason for reduction of the interlaminar peel strength is that the respective layers show different responses deformation caused from the outside and a force given from the outside, namely they differ from each other in viscoelastic characteristics, unless the layer-constituting resins are thermoplastic resins having quite the same chemical and physical properties and therefore, different stresses or strains are caused in interfaces between every two adjacent layers, resulting in reduction of the adhesive force. This undesirable phenomenon is often observed also in the case where an unsaturated carboxylic acid-modified thermoplastic resin is used as an adhesive layer between a layer of a versatile resin such as polyolefin and a layer of a high gas-barrier resin such as mentioned above.

We found that when a parison or sheet having a multi-layer structure is molded into a container, in order to enhance the transparency and interlaminar peel strength, it is important that a high oxygen-barrier resin such as mentioned above and an orienting resin such as mentioned above should be selected so that the difference ( $\Delta T$ ) between the melting or softening point ( $T_B$ ) of the high oxygen-barrier resin and the melting or softening point ( $T_G$ ) of the orienting resin is not larger than 35°C., and that at least one of two-dimensional orientation coefficients ( $I$  and  $m$ ) of at least one layer of the

Table 2

Resin	$\text{PO}_2 \times 10^{12}$ cc · cm <sup>2</sup> · sec · cmHg (at 37°C. and 0% RH)
<b>Ethylene-Vinyl Alcohol Copolymers</b>	
Vinyl alcohol content of 40 mole %	3.8
Vinyl alcohol content of 50 mole %	0.5
Vinyl alcohol content of 60 mole %	0.1

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orienting resin in a smallest-thickness portion of the final molded container should be at least 0.05.

More specifically, it was found that when the melting or softening point ( $T_B$ ) of the high barrier resin is lower than the melting or softening point ( $T_O$ ) of the orienting resin by more than 35° C., under container-molding conditions giving the above-mentioned degree of orientation, the high barrier resin is in the completely molten state and because of extreme thickness unevenness of the high barrier resin layer caused in response to the temperature distribution of the parison or sheet at the molding step or of heat generation caused by solidification or crystallization of the high barrier resin at the cooling stage after the molding step, the orientation and transparency of the orienting resin layer other than the high barrier resin layer are drastically reduced. Moreover, it was found that when the melting or softening point ( $T_B$ ) of the high barrier resin is higher than the melting or softening point ( $T_O$ ) of the orienting resin by more than 35° C., under molding conditions giving the above-mentioned degree of orientation, the high barrier resin is in the relatively viscoelastically solid state and a high stress is generated on the interface between the high barrier resin layer and the adjacent other resin layer, to cause drastic reduction of the interlaminar peel strength in the final molded container. As will be apparent from these findings, it is especially important that the high oxygen-barrier resin and orienting resin should be selected so that the difference ( $\Delta t$ ) between the melting or softening point ( $T_B$ ) of the high oxygen-barrier resin and the melting or softening point ( $T_O$ ) of the orienting resin is not larger than 35° C.

As the orienting thermoplastic resin (B), any of known thermoplastic resins capable of being oriented by drawing, other than the above-mentioned oxygen-barrier thermoplastic resin (A), can be used in this invention, so far as the above-mentioned requirements are satisfied. For example, homopolymers of olefins represented by the following formula:



(4)

wherein R stands for a hydrogen atom or an alkyl group having up to 4 carbon atoms, such as ethylene, propylene, butene-1, pentene-1 and 4-methylpentene-1, copolymers of these olefins, copolymers of these olefins with a small amount, generally 0.05 to 10% by weight based on the olefin, of other ethylenically unsaturated monomer such as vinyl acetate, an acrylic acid ester or the like, and blends of two or more of the foregoing polymers can be preferably employed for production of multi-layer parisons or sheets to be used in this invention, so far as they are crystalline. In order to obtain a molded container excellent in the rigidity and mechanical strength by draw molding, it is very important that homopolymers or copolymers of olefins should be crystalline. As the olefin homopolymer or copolymer, crystalline polypropylene is most preferred in view of the transparency and mechanical properties. In addition, there can be mentioned an ethylenepropylene copolymer, high density polyethylene, poly-4-methylpentene-1, polybutene-1 and medium density polyethylene in an order of importance. As the ethylenepropylene copolymer, a crystalline polymer comprising 0.5 to 15 mole % of ethylene and 85 to 95.5 mole % of propylene is especially valuable. In general, the olefin homopolymer or copolymer to be used should have a molecular weight

sufficient to form a film, and it is preferred that the melt index (as determined according to the method of ASTM D-1238) of the olefin homopolymer or copolymer be 0.0001 to 5, especially 0.01 to 2.5.

Another instances of the orienting thermoplastic resin include polycarbonates and thermoplastic acrylic resins. As preferred examples of the polycarbonate, there can be mentioned polymers of carbonic acid esters obtained by reaction of bisphenol with phosgene, and as preferred examples of the acrylic resin, there can be mentioned homopolymers and copolymers of acrylic acid esters and methacrylic acid esters.

In this invention, the orienting resin layer may be a layer of a blend of the orienting thermoplastic resin with other thermoplastic resin, for example, the above-mentioned oxygen-barrier resin or an adhesive resin described hereinafter, so far as the orienting thermoplastic resin is a main component. If this feature is adopted, flashes formed at the step of molding of containers can be used for formation of the orienting resin layers.

In this invention, it is preferred that the oxygen-barrier thermoplastic resin (A) and the orienting thermoplastic resin (B) be selected and combined so that the requirement represented by the following formula:

$$0.617_0 - 56.8 \leq X \leq 0.617_0 - 26.2 \quad (5)$$

wherein  $T_O$  stands for the melting or softening point (°C.) of the orienting thermoplastic resin (B) and X stands for the content (mole %) of the vinyl alcohol units in the oxygen-barrier thermoplastic resin (A), is satisfied.

In this invention, in general, it is preferred that an adhesive resin (C) having an adhesiveness to both the oxygen-barrier thermoplastic resin layer (A) and the orienting thermoplastic resin layer (B) be interposed between the two layers (A) and (B).

Any of known resins having an adhesiveness to the above-mentioned oxygen-barrier thermoplastic resin (A) and orienting thermoplastic resin (B) can be used as the adhesive resin (C). In general, however, as the adhesive polymer (C), there are employed thermoplastic polymers having carbonyl groups



derived from functional groups of free carboxylic acids, carboxylic acid salts, carboxylic acid esters, carboxylic acid amides, carboxylic anhydrides, carbonic acid esters, urethane, urea or the like. In these thermoplastic polymers, the carbonyl group concentration may be changed in a broad range, but in general, it is preferred to use a thermoplastic polymer containing carbonyl groups at a concentration of 10 to 1400 millimoles per 100 g of the polymer, especially 30 to 1200 millimoles per 100 g of the polymer. Preferred adhesive resins include polyolefins modified with at least one ethylenically unsaturated monomer selected from unsaturated carboxylic acids and anhydrides, esters and amides thereof, especially polypropylene, high density polyethylene, low density polyethylene and ethylene-vinyl acetate copolymers modified with at least one member selected from acrylic acid, methacrylic acid, crotonic acid, fumaric acid, itaconic acid, maleic anhydride,

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itaconic anhydride, citraconic anhydride, ethyl acrylate, methyl methacrylate, ethyl maleate, 2-ethylhexyl acrylate, acrylamide, methacrylamide, coconut fatty acid amide and maleimide. In addition, as the adhesive resin, there can be used ethylene-acrylate copolymers, ionomers (such as Surlyn® manufactured by Du Pont), polyalkylene oxide-polyester block copolymers, carboxymethyl cellulose derivatives, and blends of these polymers with polyolefins.

In order to draw a parison or sheet having a multi-layer structure under the above-mentioned conditions, the melting or softening point of the adhesive resin is limited.

More specifically, the melting or softening point ( $T_C$ , °C) of the adhesive resin (C) should be lower than the melting or softening point ( $T_O$ , °C) of the orienting thermoplastic resin (B), and in view of the interlaminar peel strength and moldability of a multi-layer parison or sheet to be drawn, it is preferred that the requirement represented by the following formula:

$$90^\circ C \geq T_O - T_C \geq 2^\circ C. \quad (1)$$

wherein  $T_O$  stands for the melting or softening point (°C) of the orienting thermoplastic resin (B) and  $T_C$  stands for the melting or softening point (°C) of the adhesive resin (C), be satisfied.

#### Multi-Layer Structure

The layer structure of the multi-layer container is preferably decided according to the use and physical properties of the container. For example, when the content is a non-aqueous content, a layer of a chemically inactive resin such as a polyolefin need not be used as the innermost layer, but when the content is a food or drink, it is preferred to use a polyolefin considered to be safest from the sanitary viewpoint as the innermost layer. Layer structures including an oxygen-barrier thermoplastic resin layer (designated as "A") and an orienting thermoplastic resin layer (designated as "B" or "B'") optionally with an adhesive resin layer (designated as "C"), which are preferably used in this invention, are as follows:

(i)	Two-Layer Structure: B/A	(i)
(ii)	Three-Layer Structure: B/C/A	(ii-1)
	B/A/B	(ii-2)
	B/A/B'	(ii-3)
(iii)	Four-Layer Structure: B/B'/C/A	(iii-1)
	B/C/A/C	(iii-2)
	B/C/A/C/B'	(iii-3)
(iv)	Five-Layer Structure: B/C/A/C/B	(iv-1)
	B/C/A/C/B'	(iv-2)
	(B + A + C)/C/A/C/B + A + C	(iv-3)
(v)	Six-Layer Structure: B/B'/C/A/C/B	(v-1)
	B/B + A + C)/C/A/C/B	(v-2)
(vi)	Seven-Layer Structure: B/B + A + C)/C/A/C/B + A + C/B	(vi-1)
	B/B'/C/A/C/B/B'	(vi-2)

Among these multi-layer structures, five-layer structures (iv-1), (iv-2) and (iv-3) and seven-layer structure (vi-1) are especially preferred.

It is preferred that in the above-mentioned multi-layer structure, 0.2 to 50%, especially 2 to 20%, of the

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total thickness of the final container be occupied by the oxygen-barrier resin layer (A).

Further, it is preferred that the respective resin layers be present in the multi-layer structure at the following thickness ratios:

B:A=from 1:1 to 500:1

and

B:C=from 1:1 to 500:1

#### Container

15 In the intended multi-layer draw-molded container or multi-layer solid phase pressure-formed container of the present invention, all the layers constituting the container should not necessarily be draw-molded or solid phase pressure-formed. In this invention, a resin layer in which a relatively excellent transparency cannot be obtained according to the conventional melt-molding method is draw-molded or solid phase pressure-formed. In this invention, it is important to select layer-constituting resins so that at least one of two-dimensional orientation coefficients (l and m) of at least one layer of the final container is at least 0.05.

20 The two-dimensional orientation coefficients referred to in the instant specification and appended claims can be determined according to the method described in "Polymers, vol. 15, No. 175, page 866" written by Yasunori Nishijima and published by Japanese Association of Polymers in 1966, in which by utilizing optically anisotropic characteristics of a fluorescent molecule, the degree and mode of molecular orientation of a polymer, i.e., a thermoplastic resin, caused by solid deformation or by flowing in the solution or melt state are qualitatively and quantitatively determined. When the two-dimensional orientation in the wall face of the container of this invention is considered in the light of teachings of the above literature reference, the two-dimensional orientation degrees can be quantitatively represented as follows:

$$I_{//}(\alpha) = K \phi l \cos^2 \alpha + m \sin^2 \alpha + (3/8)n \quad (2)$$

25 wherein  $I_{//}(\alpha)$  stands for the intensity of the polarized component of the fluorescence emitted from a thermoplastic resin as the sample, // indicates that the vibration direction of incident polarized light is in parallel to the direction of measured polarized light,  $\alpha$  stands for the rotation angle of the sample with respect to the vibration direction of said polarized light, K designates a maximum excitation probability when the molecular axis of the sample is in parallel to the vibration direction of excited fluorescent light,  $\phi$  stands for the molecular fluorescent contraction, l designates the ratio of orientation of the molecule in one optional direction in the wall face of the container, m designates the ratio of orientation in a direction rectangular to the orientation direction of l, n stands for the ratio of non-orientation in the wall face, and the sum of l, m and n is 1 ( $l+m+n=1$ ).

30 When the adhesive resin (C) is interposed between the oxygen-barrier resin layer (A) and the orienting resin layer (B), it is preferred that the adhesive resin layer (C) be substantially non-oriented.

35 In accordance with another preferred embodiment of this invention, there is provided a multi-layer container wherein the oxygen-barrier resin and the orienting resin

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are selected so that the requirement represented by the following formula:

$$|T_B - T_O| \leq 10^\circ C. \quad (7)$$

wherein  $T_B$  and  $T_O$  are as defined above, is satisfied, at least one of two-dimensional orientation coefficients ( $l$  and  $m$ ) of at least one layer of the orienting thermoplastic resin in a smallest-thickness portion of the container is at least 0.1, each resin layer has a haze (Hz) lower than 10%, and wherein the bonding strength between every two adjacent layer is at least 20 g/cm.

In order to obtain a container having much preferred transparency and rigidity, it is important that the difference  $\Delta t$  should be not larger than  $10^\circ C.$  and at least one of two-dimensional orientation coefficients ( $l$  and  $m$ ) should be at least 0.1. When at least one of the two-dimensional orientation coefficients of the orienting resin layer is at least 0.1, namely when the orienting resin layer is drawn at a relatively high draw ratio, there is observed a tendency that the bonding strength between adjacent layers is reduced, as pointed out hereinbefore. However, we found that if each layer constituting the container has a haze (Hz) lower than 10%, namely if each layer is excellent in the transparency, the peeling is not visually noted under shaking or falling between two adjacent layers, and that this effect can be prominently attained if the interlaminar bonding strength between every two adjacent layers is at least 20 g/cm.

The molded container of this invention has a unit volume (the volume per unit weight, g, of the resin) of 0.01 to 5 dl/g, especially 0.05 to 2 dl/g, though the unit volume is changed to some extent depending on the intended use of the container. The wall thickness of the container of this invention is adjusted in a range of from 0.02 to 1 mm, especially from 0.08 to 0.8 mm. When the unit volume and wall thickness are appropriately chosen within these ranges, a preferred combination of high interlaminar peel strength, high gas-barrier property, high rigidity and high transparency can be attained.

#### Preparation Process

The container of this invention can be prepared according to a process comprising forming a parison or sheet having the above-mentioned multi-layer structure by co-melt-extrusion, and molding the parison or sheet into a container at a molding temperature ( $T_m$ ) satisfying the requirement represented by the following formula:

$$|T_m - T_B| \leq 30^\circ C. \quad (8)$$

wherein  $T_B$  is as defined above and  $T_m$  stands for the molding temperature ( $^{\circ}C.$ ), and under such conditions that orientation of the orienting thermoplastic resin is caused at least in a smallest-thickness portion of the container.

A parison or sheet having the above-mentioned multi-layer structure can be formed by known molding means. For example, a multi-layer parison can be prepared by concurrent extrusion or injection molding of the above-mentioned resins in a layer structure as mentioned hereinbefore. Further, a multi-layer sheet can be prepared by extruding the above-mentioned resins in a multi-layer structure as mentioned hereinbefore according to known means and molding the extrudate into a sheet according to the known T-die molding method.

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The so obtained laminate sheet may be subjected to a post treatment such as rolling.

The importance that the temperature ( $T_m$ ) for molding the multi-layer parison or sheet under drawing should be in the range satisfying the requirement represented by the formula (8) will be apparent from the illustration given hereinbefore with respect to the resin components.

When the adhesive resin layer (C) is interposed between the oxygen-barrier thermoplastic resin layer (A) and the orienting resin layer (B), it also is important that the multi-layer parison or sheet should be monoaxially or biaxially draw-molded at a temperature ( $T_m$ ) higher than the melting or softening point ( $T_C$ ) of the adhesive resin (C) but lower than the melting or softening point ( $T_O$ ) of the orienting thermoplastic resin (B).

When monoaxial or biaxial draw-molding is carried out at a temperature ( $T_m$ ) satisfying the requirement represented by the following formula:

$$T_O > T_m \leq T_C \quad (9)$$

according to a preferred embodiment of this invention, drawing is effected while the orienting thermoplastic resin (B) is in the non-softened state and the adhesive resin (C) is in the molten or softened state, and while effective orientation can be given to the orienting thermoplastic resin, the interlaminar peel strength between the orienting thermoplastic resin layer (B) and the oxygen-barrier thermoplastic resin layer (A) can be remarkably enhanced. When draw-molding is carried out at a temperature lower than the melting or softening point of the adhesive resin (C), as shown in Example 7 given hereinafter (see comparative bottle BB), in the resulting draw-molded bottle, delamination is readily caused between the oxygen-barrier resin layer (A) and the orienting resin layer (B) under falling shock or the like. On the other hand, as shown in Example 7 given hereinafter, when draw-molding is carried out at a temperature higher than the melting or softening point of the orienting resin (B), a heated parison (parison will be often referred to as "pipe" hereinafter) is poor in the form-retaining property and it is readily deformed, and it sometime become impossible to perform draw-molding. If draw-molding be possible, the resulting bottle is insufficient in such properties as transparency and smoothness.

In contrast, when the multi-layer parison or sheet is draw-molded at a temperature ( $T_m$ ) higher than the melting or softening point of the adhesive resin but lower than the melting or softening point of the orienting resin according to this invention, as shown in Examples given hereinbefore, a draw-molded container excellent in such properties as rigidity, mechanical strength, transparency and smoothness can be obtained with good moldability and processability. Moreover, the interlaminar peel strength between the oxygen-barrier resin layer (A) and the orienting resin layer (B) can be enhanced to a level exceeding 135 g/cm of the width, and in the resulting container, delamination is not substantially caused under falling shock.

The reason why the interlaminar strength of the container can be prominently improved by conducting draw-molding under the above-mentioned temperature condition according to the present embodiment of this invention has not been completely elucidated, but it is construed that main causes are as follows.

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The adhesive resin (C) in the molten or softened state at the draw-molding step has an action of moderating stress or strain generated on the interface between the two resin layers at the draw-molding step, and the interposed adhesive resin (C) present in the molten or softened state promotes drawing of the orienting resin layer (B) or the oxygen-barrier resin layer (A).

Under the above-mentioned draw-molding temperature condition of this embodiment the oxygen-barrier resin layer (A) may be in the molten or softened state or in the non-molten or non-solidified state. For example, when the oxygen-barrier resin (A) is an ethylenevinyl alcohol copolymer, it is preferred that monoaxial or biaxial drawing be carried out while the copolymer is in the molten or softened state. In case of monoaxial drawing, the copolymer may be kept in the non-molten or semi-molten state. On the other hand, when the oxygen-barrier resin (A) is a polyamide resin, in general, there is not such condition.

A hot air circulating passage, an infrared heater, an induction heater, a microwave irradiator, a heater for contact with a heating medium such as steam or heated oil or a combination of these heating means can be used for maintaining the multi-layer parison or sheet at the above-mentioned draw-molding temperature ( $T_m$ ). Of course, it is possible to perform draw-molding when the temperature of an as-molded parison or sheet having the above-mentioned molded structure is lowered to the above-mentioned draw-molding temperature.

In this invention, in view of such properties as rigidity, mechanical strength and transparency of the resulting container, it is preferred that the multi-layer parison or sheet be drawn to such an extent that at least one of two-dimensional orientation coefficients ( $l$  and  $m$ ) of at least one layer of the orienting resin in a smallest-thickness portion of the container is at least 0.05.

For attaining this feature, in general, it is preferred that the draw ratio of the multi-layer parison or sheet be 1.1 to 20, especially 1.5 to 5. The drawing speed at the step of forming the multi-layer parison or sheet into a container differs depending on the kind of the resin, and the drawing speed is appropriately decided within a range causing the above-mentioned drawing effect. It is especially preferred that the drawing speed be in a range of from 10%/mm to 6,000,000%/mm.

In this invention, draw-molding of the multi-layer parison or sheet into a container can be performed under the same conditions as known molding conditions except that the molding temperature ( $T_m$ ) is maintained within the above-mentioned range and drawing is carried out to such an extent that at least one of two-dimensional orientation coefficients ( $l$  and  $m$ ) is at least 0.05, especially at least 0.1.

For example, formation of a bottle from the multi-layer parison can be accomplished by drawing of the parison in the axial direction by holding means or a mandrel and drawing of the parison in the lateral direction by blow-in of a fluid. Steps of drawing the parison in the axial direction and in the lateral direction may be conducted concurrently or in sequence.

Formation of a container such as a cup from the multi-layer sheet can be accomplished by plug-assist forming (vacuum molding), air-pressure forming, sheet blow molding, draw forming, draw-ironing molding, compression molding, forward extrusion, backward extrusion, forward-backward extrusion and explosion forming. In the instant specification, these forming

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methods are collectively called "draw forming method".

When draw-molding is carried out under the above-mentioned conditions according to this invention, a container excellent in transparency, rigidity and gas-barrier property and having especially high interlamellar peel strength can be obtained. Further, by virtue of the drawing effect, it is made possible to reduce the wall thickness of the container, decrease the weight of the container and reduce amounts used of resins drastically.

#### Uses

The container of this invention has a desirable combination of gas-barrier property, rigidity, transparency and interlamellar peel strength, and they can be valuably applied to various uses.

Because of these advantages, the container of the present invention is very useful for preserving, without substantial deterioration or quantity loss, various liquid and pasty foods and drinks, for example, bubbling alcoholic drinks such as beer, other alcoholic drinks such as Japanese sake, whisky, distilled spirits, wines, gin fizz and other cocktails, carbonated drinks such as cola, cider and plain soda, fruit drinks such as straight fruit juices, e.g., lemon juice, orange juice, plum juice, grape juice and strawberry juice and processed fruit juices, e.g., Nector (R), vegetable juices such as tomato juice, synthetic drinks and vitamin-incorporated drinks formed by blending a saccharide such as sugar or fructose, citric acid, a colorant and a perfume optionally with vitamins, lactic acid beverages, stews, e.g., pre-cooked curry, pre-cooked hash, borsch and beef stew, gravy, e.g., meat sauce, boiled vegetables, fishes and meats, e.g., vinegar-cooked pork, sukiyaki, Chinese food paste of beef and vegetables, Chinese hotchpotch, boiled spinach, boiled mushroom, boiled asparagus, boiled beans, boiled corn and cream-boiled tuna, soups, e.g., consomme soup, potage soup, miso soup, pork-incorporated miso soup and vegetable soup cooked with oil, rice foods, e.g., boiled rice, rice boiled with red beans, toasted boiled rice, frizzled boiled rice, pilaff and rice-gruel, noodles, e.g., spaghetti, buck-wheat vermicelli, wheat vermicelli, Chinese noodle and Italian noodle, compound condiments, e.g., those for toasted boiled rice or Chinese noodle soup, luxury foods, e.g., tasted boiled red beans, thick and thick bean-meal soups with sugar, sugared and boiled beans with rice cake or fruits and jelly, boiled beans with treacle poured on, custard pudding, jelly cakes and soft adzuki-bean jelly, processed fish and meat products, e.g., meat dumpling, hamburger, corn beef, ham, sausage, roast fish, smoked fish, bacon and boiled fish paste, fruit products, e.g., processed orange, peach, pine-apple, cherry and apple, condiments such as soy, sauce, vinegar, sweet sake, dressing, mayonnaise, ketchup, soybean paste, lard and edible oil, and foods such as bean curd, jam, butter and margarine; liquid medicines, liquid agricultural chemicals, liquid cosmetics and detergents; ketones such as acetone and methylethyl ketone; aliphatic hydrocarbons such as n-hexane and n-heptane; alicyclic hydrocarbons such as cyclohexane; aromatic hydrocarbons such as benzene, toluene and xylene; chlorine-containing carbon tetrachloride, tetrachloroethane and tetrachloroethylene; liquid fuels and oils such as gasoline, kerosine, petroleum bendine, fuel oil, thinner, grease, silicone oil, light oil and machine oil; and liquefied Freon (the trademark of a product manufactured by DuPont).

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This invention will now be described by reference to the following Examples that by no means limit the scope of the invention.

## EXAMPLE 1

Parisons having both the ends opened and having an inner diameter of 10 mm, a length of 185 mm and a thickness of 7.5 mm and parisons having both the ends opened and having an inner diameter of 15 mm, a length of 100 mm and a thickness of 4.5 mm were prepared from the following 24 combinations of innermost and outermost layers, intermediate layers and adhesive layers by using an extruder for forming innermost and outermost layers, which included a full-flighted screw having a diameter of 65 mm and an effective length of 1430 mm and was provided with a melt channel divided into two flow passages, an extruder for forming adhesive layers, which included a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm and was provided with a melt channel divided into two flow passages, an extruder for forming intermediate layers, which included a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm, a 5-ply die, a pipe former and a pipe cutter.

Resins used for formation of intermediate layers are as follows:

EV1:

Ethylene-vinyl alcohol copolymer having an ethylene content of 45 mole %, a vinyl alcohol content of 55 mole %, a melting point of 154° C. as measured according to the differential thermal analysis method (hereinafter referred to as "DTA method") in which the temperature-elevating rate was 10° C./min. and an oxygen permeability ( $\text{PO}_2$ ) of  $0.23 \times 10^{-12} \text{ cc-cm/cm}^2\text{-sec-cmHg}$  as measured at a temperature of 37° C. and a relative humidity of 6%.

EV2:

Ethylene-vinyl alcohol copolymer having an ethylene content of 39 mole %, a vinyl alcohol content of 70 mole %, a melting point of 181° C. as measured according to the above-mentioned DTA method and an oxygen permeability of  $0.07 \times 10^{-12} \text{ cc-cm/cm}^2\text{-sec-cmHg}$  as measured under the above-mentioned conditions.

EV3:

Ethylene-vinyl alcohol copolymer having an ethylene content of 19 mole %, a vinyl alcohol content of 81 mole %, a melting point of 197° C. as measured according to the above-mentioned DTA method and an oxygen permeability of  $0.059 \times 10^{-12} \text{ cc-cm/cm}^2\text{-sec-cmHg}$  as measured under the above-mentioned conditions.

EV4:

Ethylene-vinyl alcohol copolymer having an ethylene content of 66 mole %, a vinyl alcohol content of 34 mole %, a melting point of 120° C. as measured according to the above-mentioned DTA method and an oxygen permeability of  $5.4 \times 10^{-12} \text{ cc-cm/cm}^2\text{-sec-cmHg}$  as measured under the above-mentioned conditions.

Resins used for formation of innermost and outermost layers are as follows:

PP1:

Isotactic polypropylene having a density of 0.909 g/cc and a melting point of 159° C. as measured according to the above-mentioned DTA method.

PP2:

Ethylene-propylene random copolymer having a density of 0.90 g/cc, a melting point of 154° C. as measured according to the above-mentioned DTA method and an ethylene content of 10 mole %.

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Resins used for formation of adhesive layers are as follows:

AH1:

Unsaturated carboxylic acid-modified polypropylene having a density of 0.90 g/cc and a melting point of 159° C. as measured according to the above-mentioned DTA method.

AH2:

Unsaturated carboxylic acid-modified polypropylene having a density of 0.90 g/cc and a melting point of 154° C. as measured according to the above-mentioned DTA method.

AH3:

Resin blend having a density of 0.90 g/cc and being composed of unsaturated carboxylic acid-modified polyethylene having a melting point of 105° C. as measured according to the above-mentioned DTA method and an unsaturated carboxylic acid-modified polypropylene having a melting point of 155° C. as measured according to the above-mentioned DTA method.

These pipes (parisons) were heated for about 30 minutes in a hot air-circulated oven maintained precisely at an atmosphere temperature of 155° C. Then, pipes having an inner diameter of 10 mm, a length of 185 mm and a thickness of 4.5 mm were formed into bottles having a thickness of 0.6 mm, an inner capacity of 300 cc and a weight of 22 to 24 g/bottle according to the sequent biaxial draw-blowing method at a draw ratio of 3 in the longitudinal direction (the bottle height direction) and at a draw ratio of 3.5 in the lateral direction (the bottle circumference direction). Bottles having the same dimensions as described above were prepared from pipes having an inner diameter of 15 mm, a length of 100 mm and a thickness of 4.5 mm according to the same sequent biaxial draw-blowing method at a draw ratio of 1.5 in the longitudinal direction and at a draw ratio of 1.5 in the lateral direction.

For comparison, cylindrical multi-layer bottles having the same dimensions as described above were prepared from some of 24 combinations according to the known direct blow-molding method (blow-molding of molten parisons) in which multi-layer parisons are extruded from the 5-ply die and in the molten state were immediately blow-molded.

In each case, the molding was carried out carefully so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:1:3 as possible.

With respect to each of the so prepared 58 kinds of bottles, the oxygen transmission rate ( $\text{QO}_2$ ), the haze ( $H_2$ ) and the orientation coefficients ( $I$ ,  $m$  and  $a$ ) of the innermost and outermost layers were determined according to the method disclosed in Japanese Patent Application Laid-Open Specification No. 49379/75, the measuring method of JIS K-6714 and the above-mentioned fluorescence method, respectively. Further, with respect to each kind of bottles, 10 sample bottles were chosen and 340 g of an aqueous solution of table salt was filled in each bottle. Then, the filled bottles were allowed to stand in an atmosphere maintained at -1° C. over 3 days and nights, and immediately, they were let to fall on a concrete floor from a height of 1.2 m in an atmosphere maintained at 20° C. so that bottle bottoms were caused to hit on the concrete floor. Then, the falling strength represented by the following formula:

$$F_s = 100 \times (10 - F_f)/10$$

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wherein  $F_1$  stands for the number of bottles broken at the first falling test and  $F_2$  denotes the falling strength, was determined. Further, occurrence of delamination was visually examined by a panel of 5 men (the occurrence of delamination was evaluated based on an average value of the number  $N$  of bottles where delamination took at the first falling test). From each bottle, specimens having a width of 10 mm and a length of 50 mm were cut off in both the vertical direction and circumferential direction of the bottle wall, and the peel strength (AT) was measured at a peeling rate of 100 mm/min in an atmosphere maintained at a temperature of 20° C. and a relative humidity of 60%. Results of these tests are shown in Table 3.

In Table 3, symbols of bottles are expressed by numbers of four figures. The thousands digit indicates the material of the intermediate layer. For example, "1", "2", "3" and "4" indicate EV1, EV2, EV3 and EV4, respectively. Similarly, the hundreds digit indicates the material of the adhesive layer and the tens digit indicates the material of the outermost and innermost layers, and the expression manner is the same as in case of the intermediate layer. The units digits indicate kinds of bottles. More specifically, "1", "2" and "3" represent a draw-blow molded bottle drawn at a draw ratio of 1.5 in the longitudinal direction and at a draw ratio of 1.5 in the lateral direction, a draw-blow molded bottle drawn

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at a draw ratio of 3.5 in the lateral direction and at a draw ratio of 3 in the longitudinal direction, and a comparative bottle formed by the above-mentioned direct blow-molding method, respectively. For example, symbol 2122 indicates a biaxially drawn blow-molded bottle comprising an intermediate layer of EV2, an adhesive layer of AH1 and innermost and outermost layers of PP1, in which the draw ratio in the lateral direction is 3.5 and the draw ratio in the longitudinal direction is 3.

From the results shown in Table 3, it will readily be understood that biaxially drawn blow-molded bottles are apparently excellent over directly blow-molded bottles with respect to the oxygen barrier property and transparency, and that although the directly blow-molded bottles are excellent over biaxially drawn blow-molded bottles with respect to the adhesion strength, the latter bottles are excellent over the former bottles with respect to the interlaminar peel strength determined by the visual test, namely the practical peel strength. It will also be understood that if the intermediate layer excellent in the barrier property to gases such as oxygen is selected so that the above-mentioned requirements of this invention are satisfied, the oxygen-barrier property, transparency and interlaminar peel strength can be remarkably improved in the resulting container.

Table 3

Symbol of Bottle	QO <sub>b</sub> cc/m <sup>2</sup> . day . atm	Layer	Hr[%]		Orientation Co-efficients (innermost and outermost layers)		
			Intermediate Layer	Adhesive Layer	Bottle	1	m
1111	7.3	<1	13	14	0.11	0.12	0.77
1112	6.0	<1	7	8	0.23	0.32	0.45
1113	8.0	<2	30	33	0.02	0.03	0.95
1121	7.2	<1	12	13	0.07	0.09	0.84
1122	6.1	<1	6	6	0.15	0.19	0.66
1123	9.0	<2	23	24	0.03	0.02	0.95
1211	7.2	<1	12	13	0.09	0.10	0.81
1212	6.2	<1	7	7	0.22	0.31	0.47
1213	8.1	<2	31	33	0.01	-0.02	0.97
1221	7.1	<1	13	14	0.09	0.11	0.89
1222	6.1	<1	6	7	0.14	0.18	0.68
1223	8.2	<2	22	23	0.03	0.04	0.93
1311	7.2	<1	14	15	0.15	0.14	0.71
1312	6.4	<1	7	8	0.21	0.25	0.54
1313	8.1	<2	31	32	0.02	0.03	0.95
1321	7.3	<1	12	12	0.08	0.08	0.84
1322	6.4	<1	6	6	0.13	0.18	0.69
1323	8.0	<2	24	25	0.01	0.04	0.95
2111	2.4	<1	13	15	0.10	0.11	0.79
2112	2.1	<1	7	9	0.25	0.32	0.43

Symbol of Bottle	Falling Test		Peel Strength (g/cm of width)	
	F <sub>b</sub> (%)	(number of bottles)	Vertical direction of bottle	Circumferential direction of bottle
1111	90	1	126	132
1112	100	0	32	40
1113	40	2	221	230
1121	100	0	151	158
1122	100	0	29	38
1123	70	1	230	241
1221	90	0	131	140
1212	100	0	22	31
1213	40	1	218	221
1221	100	1	142	153
1222	100	0	63	72
1223	70	2	292	291
1311	80	0	141	150
1312	100	0	49	53
1313	40	1	289	293
1321	100	0	150	163
1322	100	0	78	84
1323	80	0	213	216

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Table 3-continued

2111	90	0	143	161
2112	100	0	38	73

Symbol of Bottle	QO <sub>2</sub> cc/m <sup>2</sup> , day, atm.	Interme- diate Layer	H <sub>d</sub> [%]		Orientation Co-efficients (innermost and outermost layers)		
			Adhesive Layer	Bottle		I	m
2113	28	<1	30	32	0.02	0.03	0.95
2121	23	<1	12	13	0.08	0.09	0.83
2122	22	<1	6	7	0.14	0.19	0.67
2123	29	<1	23	25	0.02	0.03	0.93
2211	24	<1	11	12	0.09	0.09	0.82
2212	22	<1	7	7	0.21	0.28	0.51
2213	31	<1	30	32	0.02	0.03	0.95
2221	23	<1	12	13	0.08	0.08	0.84
2222	21	<1	6	7	0.15	0.20	0.65
2223	29	<1	22	23	0.01	0.04	0.95
2311	22	<1	14	15	0.10	0.08	0.82
2312	20	<1	7	8	0.28	0.32	0.40
2321	29	<1	12	14	0.09	0.08	0.83
2322	21	<1	6	7	0.14	0.20	0.66
3111	35.0	<1	13	15	0.11	0.09	0.80
3112	35.0	<1	7	7	0.24	0.27	0.47
3121	21	<1	12	13	0.08	0.09	0.83
3122	19	<1	6	7	0.14	0.20	0.66
3211	20	<1	11	13	0.10	0.09	0.81
3212	21.0	<1	7	8	0.24	0.28	0.48

Symbol of Bottle	Falling Test		Peel Strength (p/cm of width)		Orientation Co-efficients (innermost and outermost layers)
	F <sub>b</sub> [%]	(number of bottles)	Vertical direction of bottle	Circumferential direction of bottle	
2113	40	1	291	301	
2121	100	0	150	158	
2122	100	0	59	76	
2123	70	2	253	254	
2211	90	0	146	153	
2212	100	0	53	72	
2213	36	1	239	293	
2221	100	0	151	161	
2222	100	0	59	73	
2223	60	1	291	293	
2311	100	0	145	146	
2312	100	0	52	63	
2321	100	0	138	151	
2322	100	0	72	71	
3111	90	1	109	113	
3112	100	2	19	19	
3121	100	1	111	116	
3122	100	2	20	19	
3211	80	1	99	103	
3212	100	1	17	21	

Symbol of Bottle	QO <sub>2</sub> cc/m <sup>2</sup> , day, atm.	Interme- diate Layer	H <sub>d</sub> [%]		Orientation Co-efficients (innermost and outermost layers)		
			Adhesive Layer	Bottle		I	m
3221	2.0	<1	12	14	0.07	0.08	0.85
3222	2.2	<1	6	7	0.15	0.19	0.66
3311	1.9	<1	14	15	0.12	0.11	0.77
3312	24.0	<1	7	7	0.21	0.27	0.52
3321	2.1	<1	12	15	0.09	0.09	0.82
3522	53.0	<5	6	7	0.14	0.018	0.68
4111	95.0	<5	15	17	0.10	0.11	0.79
4112	74.2	<5	11	12	0.21	0.27	0.52
4121	91.0	<5	13	15	0.08	0.09	0.83
4122	26.0	<5	10	12	0.14	0.16	0.70
4211	83.0	<5	14	15	0.12	0.11	0.77
4212	80.0	<5	11	13	0.23	0.31	0.46
4221	91.0	<5	14	16	0.09	0.08	0.83
4222	71.2	<5	11	12	0.15	0.23	0.62
4311	86.5	<5	15	17	0.13	0.11	0.76
4312	72.4	<5	12	14	0.22	0.24	0.44
4321	91.3	<5	15	16	0.08	0.09	0.63
4322	70.7	<5	10	12	0.14	0.22	0.64

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Table 3-continued

Symbol of Bottle	Falling Test  FB (%)	(number of bottles)	Peel Strength (g/cm of width)	
			Vertical direction of bottle	Circumferential direction of bottle
3221	100	1	113	116
3222	100	2	21	23
3311	80	1	103	106
3312	90	1	19	21
3321	100	2	139	148
3322	100	2	21	23
4111	90	2	117	121
4112	100	1	31	29
4121	100	2	117	118
4122	100	2	29	33
4211	90	1	119	123
4212	100	1	31	42
4221	100	0	120	131
4222	100	1	41	52
4311	80	1	125	128
4312	100	0	51	62
4321	90	0	131	130
4322	100	1	61	59

## EXAMPLE 2

Symmetric 5-layer sheets having a thickness of 0.8 mm and a width of 450 mm were formed by using an extruder for forming innermost and outermost layers, which included a full-flighted screw having a diameter of 65 mm and an effective length of 1430 mm, an extruder for forming adhesive layers, which included a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm, an extruder for forming intermediate layers, which included a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm, a T-die equipped with a multi-channel adaptor and having a lip width of 0.6 mm and a lip length of 500 mm, and a sheet-forming machine. The ethylene-vinyl alcohol copolymers EV1, EV2, EV3 and EV4 described in Example 1 were used as the intermediate layer-constituting material. An ethylene-propylene copolymer having a density of 0.9 g/cc, a melting point of 156° C. as measured according to the DTA method, a melt index of 1.6 dg/min as measured according to the method of JIS K-6758 and an ethylene content of 10 mole % was used as the material of the innermost and outermost layers. An unsaturated carboxylic acid-modified ethylene-propylene copolymer having a density of 0.90 g/cc, a melting point of 154° C. as measured according to the DTA method and a melt index of 2.0 dg/min as measured according to the above-mentioned method was used as the adhesive layer-constituting material. The sheet forming operation was carried out by adjusting the amounts of resins extruded from the three extruders so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:1:3 as possible. The so formed 4 kinds of sheets were heated for about 15 minutes in a hot air-circulated oven having an atmosphere maintained precisely at 155° C. and they were formed into cups having a diameter of 85 mm, a height of 50 mm, an inner capacity of 300 cc and a unit weight of 9 to 10 g/cup according to the plug assist vacuum forming method disclosed in the specification of co-pending U.S. Application Ser. No. 750,376.

For comparison, cylindrical cups having the same dimensions as described above were formed from the 65 above-mentioned 4 kinds of sheets according to the

conventional sheet-blown method, in which the sheets as-extruded from the T-die and in the molten state were blow-molded.

Cups formed according to the plug assist vacuum forming method (solid phase forming method) using EV1 as the intermediate layer are designated as "SP1", and cups formed by the molten sheet blow-molding method using EV1 are designated as "SB1". Similarly, cups formed by using EV2, EV3 and EV4 according to the plug assist vacuum forming method are designated as "SP2", "SP3" and "SP4", respectively, and cups formed by using EV2, EV3 and EV4 according to the molten sheet blow-molding method are designated as "SB2", "SB3" and "SB4", respectively.

With respect to each of the foregoing 8 kinds of cups, the oxygen transmission rate ( $QO_2$ ), the haze (Hz) and the orientation coefficients ( $I$ ,  $m$  and  $n$ ) were determined according to the methods described in Example 1. Further, 10 sample cups were chosen from each kind of cups, and 340 g of an aqueous solution of table salt was filled in each cup. The filled cups were allowed to stand in an atmosphere maintained at -1° C. over 3 nights and days, and immediately, the cups were subjected to the free vibration test under conditions of a vibration frequency of 400 cpm, a vibration amplitude of 20 mm and an acceleration of 1.8 G for 30 minutes by using a Matsudaira type vibration tester and the number (N) of broken cups were counted. Further, occurrence of delamination was visually tested by a panel of 5 men (the occurrence of delamination was evaluated based on an average number (ADN) of cups where delamination took place). The thickness unevenness of the intermediate layer in molded cups was examined in both the vertical and circumferential direction of the cup and standard deviations  $\delta L$  and  $\delta H$  were determined. Results of these tests are shown in Table 4.

As will appear from the results shown in Table 4, the solid phase pressure-formed cups are excellent over directly melt-molded cups with respect to the oxygen-barrier property and transparency. It will also be understood that if the intermediate layer is selected so that the requirements of this invention are satisfied, the resulting cups (samples SP1 and SP2) are much excellent in the interlamellar peel strength and the thickness uniformity of the intermediate layer.

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Table 4

Symbol of Cap	$QO_2$ cc/m <sup>2</sup> . day. atm	Interme- diate Layer	Hz[%]		Orientation Coefficients (innermost and outermost layers)		
			Adhesive Layer	Cap	I	m	n
SP1	8.3	<1	7	8	0.31	0.13	0.56
SP2	3.1	<1	6	7	0.41	0.09	0.50
SP3	3.0	<1	6	7	0.29	0.15	0.56
SP4	43.2	<1	16	18	0.32	0.15	0.53
SB1	13.2	<2	23	24	0.03	0.01	0.96
SB2	10.1	<2	22	22	0.04	0.02	0.94
SB3	9.6	<2	21	22	0.02	0.01	0.97
SB4	14.2	<2	23	24	0.03	0.01	0.96

Symbol of Cap	Results of Vibration Test		Thickness Unevenness of Intermediate Layer	
	N	ADN	$\delta L$	$\delta H$
SP1	0	0	0.20	-0.09
SP2	0	0	0.15	0.09
SP3	0	2	0.23	0.10
SP4	0	1	0.62	0.31
SB1	0	1	0.21	0.13
SB2	1	1	0.22	0.12
SB3	0	2	0.20	0.15
SB4	1	3	0.21	0.11

## EXAMPLE 3

By using the same molding equipment as used in Example 1, symmetric five-layer parisons composed of three kinds of resins were prepared, and bottles having a symmetric 5-layer structure were formed from these parisons according to the sequent biaxial draw-blow forming method in which the drawing operation was carried out at 159°C. at a draw ratio of 3 in the longitudinal direction and at a draw ratio of 3.5 in the lateral direction. An  $\alpha$ -aminocaproic acid polymer (N1) having a melting point of 223°C. as measured according to the DTA method, a relative viscosity of 1.9 as measured with respect to a solution of 1 g of the polymer in 100 cc of 98% concentrated sulfuric acid and an oxygen permeability of  $4.0 \times 10^{-12}$  cc·cm/ $\text{cm}^2\text{sec}\text{-cmHg}$  as measured at a temperature of 37°C. and a relative humidity of 0% and a caprolactam/hexamethylene diaminon adipate copolymer (N2) having a melting point of 163°C. as measured according to the DTA method, a relative viscosity of 3.4 as measured in the same manner as described above, an oxygen permeability of  $3.5 \times 10^{-12}$  cc·cm/ $\text{cm}^2\text{sec}\text{-cmHg}$  as measured in the same manner as described above and a caprolactam concentration of 81 mole % were used as the intermediate layer-constituting material. An unsaturated carboxylic acid-modified polypropylene having a density of 0.90 g/cc and a melting point of 156°C. as measured according to the DTA method was used as the material of the adhesive layer adjacent to the intermediate layer. An isotactic polypropylene having a density of 0.909 g/cc and a melting point of 160°C. as measured according to the DTA method was used as the material constituting the innermost and outermost layers.

For comparison, with respect to each of the foregoing two combinations of resins, in the same manner as described in Example 1, bottles were formed from multi-layer parisons extruded from the 5-ply die and still in

the molten state according to the direct blow molding method.

Configurations of the so formed 4 kinds of bottles were the same as those described in Example 1. The amounts of resins extruded from the three extruders were adjusted so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:2:1 as possible.

With respect to each of these 4 kinds of bottles, the oxygen transmission rate ( $QO_2$ ), haze (Hz), orientation coefficients, falling strength (Fz) and interlaminar peel strength were determined according to the same methods as described in Example 1, and the number (N) of broken bottles and occurrence of delamination at the vibration test and the standard deviations  $\delta L$  and  $\delta H$  indicating the thickness unevenness of the intermediate layer were determined according to the same methods as described in Example 2. Results of these tests are shown in Table 5. In Table 5, bottle symbols indicate the following bottles:

BO1:

Biaxially drawn blow-formed bottles containing N1 as the intermediate layer-constituting material.

BO2:

Biaxially drawn blow-formed bottles containing N2 as the intermediate layer-constituting material.

DO1:

Directly blow-molded bottles (formed by blow molding of molten parisons) containing N1 as the intermediate layer-constituting material.

DO2:

Directly blow-molded bottles containing N2 as the intermediate layer-constituting material.

From the results shown in Table 5, it will readily be understood that BO2 bottles formed by selecting the intermediate layer so that the requirements of the present invention are satisfied are much excellent in the oxygen-barrier property, falling strength, strength and delamination resistance at the vibration test and thickness uniformity of the intermediate layer.

Table 5

Hz[%]

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Table 3-continued

Symbol of Bottle	O <sub>2</sub> , cc/m <sup>2</sup> . dry atm	Interme- diate Layer	Innermost and Outermost Layers plus Adhesive Layer		Bottle	Orientation Coefficients (innermost and outermost layers)		
			I	M		N		
BO1	56.2	<2	7	8	0.23	0.31	0.46	
BO2	19.1	<2	6	7	0.22	0.30	0.48	
DO1	41.5	<5	31	33	0.02	0.01	-0.97	
DO2	36.9	<5	32	34	0.03	0.02	0.95	

Symbol of Bottle	Falling Test Results		Vibration Test Results		Thickness Unevenness of Intermediate Layer	
	FB (%)	N (number of broken bottles)	N	ADN	δL	δH
BO1	100	3	0	1	0.35	0.12
BO2	100	0	0	0	0.15	0.09
DO1	40	0	0	0	0.21	0.10
DO2	50	1	1	1	0.20	0.11

## EXAMPLE 4

Sheets having a thickness of 0.5 mm and a width of about 400 mm and having a symmetric 5-layer structure were prepared by using a known extruding and sheet-forming machine.

The same  $\omega$ -aminocaproic acid polymer (6-nylon, NI) as used in Example 3, 6,6-nylon (N3) having a melting point of 265° C. according to the DTA method in which the temperature-elevating rate was 10° C./min and an oxygen permeability of  $0.69 \times 10^{-12}$  cc·cm/ $\text{cm}^2\text{-sec-cmHg}$  as measured at a temperature of 37° C. and a relative humidity of 0%, and an 80/20 (weight ratio) mixture (N13) of 6-nylon and 6,6-nylon having a melting point of 228° C. as measured according to the above DTA method and an oxygen permeability of  $2.2 \times 10^{-12}$  cc·cm/ $\text{cm}^2\text{-sec-cmHg}$  were used as the intermediate layer-constituting resin. A 4-methyl-pentene-1 polymer (manufactured and sold under trademark "TPX" by ICI) having a density of 0.835 g/cc, a melting point of 228° C. as measured according to the above DTA method and a melt index of about 7.0 as measured under conditions of a load of 5 Kg. and a temperature of 265° C. was used as the resin constituting innermost and outermost layers. Adhesive polypropylene (manufactured and sold under trademark "MODIC" by Mitsubishi Petrochemical) having a density of 0.90 g/cc, a melting point of 153° C. as measured according to the above DTA method and a melt index of 2.4 as measured according to the method of JIS K-6760 was used as the resin constituting an adhesive layer interposed between the innermost or outermost layer and the intermediate layer. In the same manner as described in Example 2, the sheet-forming operation was carried out while adjusting the rotation number of the screw so that the innermost or outermost layer/adhesive layer/intermediate layer thickness ratio was as close to as 100:5:10 as possible.

The so prepared three kinds of sheets were sufficiently heated in a hot air-circulated oven installed with

an infrared heater maintained precisely at a molding temperature indicated in Table 6, and they were formed into cylindrical cups having a diameter of 85 mm, a height of 50 mm, an inner capacity of 300 cc and a unit weight of 9 to 10 g per cup according to the known plug assist air-pressure forming method.

For comparison, the foregoing three kinds of sheets were heated at 250° C. in the above-mentioned oven just after formation of the sheets and they were formed into cylindrical cups having the same configurations as described above according to the plug assist air-pressure forming method.

With respect to each of the so obtained 6 kinds of cups, the peel strength, the thickness unevenness in both the vertical and circumferential directions of the cup and the standard deviations  $\delta L$  and  $\delta H$  were determined to obtain results shown in Table 6.

As will be apparent from the results shown in Table 6, as compared with the normal heat forming method conducted at 265° C., in the solid phase pressure forming method conducted at 226° C., resin combinations satisfying the requirements of the present invention give generally better results.

In the above-mentioned DTA method, the melting-initiating temperature (the temperature at which melting endotherm takes place in the DTA thermogram) of 6-nylon (NI) was 209° C. and the melting-ending temperature (the temperature at which melting endotherm is completed in the DTA thermogram) was 229° C. The melting-initiating temperature of the blend (N13) of 6-nylon and 6,6-nylon was 203° C. and the melting-ending temperature of the nylon blend was 232° C. The melting-initiating and melting-ending temperatures of 6,6-nylon were 246° C. and 268° C., respectively. Accordingly, when the forming was carried out at 226° C., 6-nylon (NI) and nylon blend (N13) were in the semi-molten state and 6,6-nylon was maintained at the forming step at a temperature much lower than the melting-initiating temperature (246° C.).

Table 6

Intermediate Layer-Consti- tuting Material	Forcing Temperature (°C.)	Interme- diate layer-adhesive layer	Peel Strength (g/1 cm width)		
			Adhesive layer-innermost or outermost layer	Thickness δL	Thickness δH
NI	226	935	410	0.15	0.09
N3	226	15	20	0.20	0.12
N13	226	930	420	0.13	0.10
NI	268	930	420	0.42	0.12
N3	268	1030	380	0.50	0.11

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Table 6-continued

Intermediate Layer-constituting Material	Forming Temperature (°C.)	Intermediate layer	Adhesive layer-innermost or outermost layer	Peel Strength (g/cm width)	
				Thickness 8L	Unevenness 8H
N13	268	920	490	0.43	0.15

EXAMPLE 5  
Four kinds of sheets prepared in Example 2 were

10 peel strength between the intermediate and adhesive layers and the haze, are lowered to levels before rolling.

Table 7

Sheet	Intermediate Layer	Tray-Forming Temperature (°C.)	Peel Strength <sup>a</sup> (g/cm width)	Orientation Coeff. <sup>b</sup> ( clients (innermost and outermost layers))			Haze (Hz) (%)
				intermediate layer-adhesive layer	adhesive layer-innermost or outermost layer	I	m
Uerolled Sheet	EV1	285	not peeled	0.02	0.01	0.97	21
	EV2	320	-	0.01	0.01	0.96	20
	EV3	430	-	0.02	0.01	0.97	21
	EV4	290	-	0.03	0.02	0.95	19
Cold-Rolled Sheet	EV1	420	-	0.20	0.08	0.72	12
	EV2	525	-	0.21	0.07	0.72	13
	EV3	930	-	0.21	0.06	0.73	11
	EV4	390	-	0.20	0.05	0.75	15
	EV1	155	415	-	0.38	0.16	0.44
	EV2	155	520	-	0.45	0.13	0.40
	EV3	155	<10***	-	0.35	0.18	0.47
	EV4	155	395	-	0.37	0.17	0.46
	EV1	210	283	-	0.03	0.02	0.95
	EV2	210	316	-	0.03	0.02	0.95
	EV3	210	450	-	0.02	0.01	0.95
	EV4	210	310	-	0.03	0.01	0.96

## Notes

<sup>a</sup>: average value (sample number = 10)  
<sup>b</sup>: I direction designates the rolling direction of the starting sheet, which corresponds to the direction of the long axis of the rectangular shape of the tray.

\*\*\*: delamination was caused between the intermediate and adhesive layers of the tray.

subjected to cold rolling at a rolling speed of about 5 m/min at room temperature by using a roll. The sheet thickness after the cold rolling was about 0.40 mm. The 40 cold-rolled sheets were heated at a tray-forming temperature precisely controlled to a level indicated in Table 7 and then formed in rectangular trays having a length of 140 mm, a width of 100 mm and a depth of 25 mm under a forming pressure of 5 to 9 Kg/cm<sup>2</sup> according to the known plug assist air-pressure forming method.

For comparison, the foregoing 4 kinds of cold-rolled sheets were sufficiently heated at about 210° C. and formed in rectangular trays having the same dimensions as described above according to the plug assist air-pressure forming method.

With respect to each of the foregoing 4 kinds of sheets before cold rolling, the foregoing 4 kinds of cold-rolled sheets and the foregoing 8 kinds of formed trays, in the same manner as described in Example 1, the peel strength and orientation coefficients (I, m and n) were determined. With respect to each of the foregoing 8 kinds of trays, the haze (Hz) was determined according to the method of JIS K-6714. Results are shown in Table 7.

As will be apparent from the results shown in Table 7, even when rolled sheets are formed into trays, if the requirements of the present invention are satisfied, the properties of trays can be remarkably improved. It will also be understood that even if properties are improved by rolling, when normal heat forming is conducted on rolled sheets, the improved properties, for example, the

## EXAMPLE 6

Symmetric 7-layer sheets composed of four resins were prepared from the same resin combination as that used in Example 1 for formation of innermost, outermost, intermediate and adhesive layers, and additionally, sheet scraps formed at the forming step in this Example and scraps formed by crushing defective cups formed in this Example by a crusher were used as the resin material for formation of layers interposed between the innermost layer and adhesive layer and between the outermost layer and adhesive layer. From these resin materials, symmetric 7-layer sheets having a thickness of about 0.8 mm and a width of 450 mm were molded by using the same extruder for formation of innermost and outermost layers, the same extruder for formation of adhesive layers, the same extruder for formation of intermediate layers and the same sheet-winding machine as used in Example 2, and additionally, an extruder for formation of intervening layers, which was installed with a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm, and a sheet extrusion molding machine comprising a multi-channel adaptor and a T-die having a lip width of 0.8 mm and a lip length of 500 mm were used for the sheet-forming operation. The screw rotation numbers of the four extruders were adjusted so that in the molded sheets, the thickness ratio of innermost or outer-